THERMAL ANALYSIS OF THE CATALYTIC ACTION OF COLLOIDS. (I)*

Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.

By Eiji Suito.

Bredig and his collaborators[1] first made comprehensive researches on the catalytic action by various colloidal solutions. They called the action of hydrosol of metal or metal oxide and hydroxide "Anorganische Fermente" because of the similarity of the action to that of enzyme. Since then, numerous investigations have been made and most of them done concerning the catalytic decomposition of hydrogen peroxide by colloidal platinum.[2] In all of these studies chemical analysis such as titration of the solution or the measurement of the evolved oxygen has been adopted for the determination of the reaction velocity. The present author investigated the said reaction by the thermo-analytical method[3], which originated with Prof. S. Horiba and was successfully applicable for continued measurements of the reaction velocity, especially for the initial part of the reaction, in order to elucidate the mechanism of the decomposition and colloidal catalysis.

Experimental.

Materials.

The platinum sol was prepared by Bredig's electric dispersion method, using a direct current (40 volts, 6 amperes) cooled in an ice-bath. After about 1 hour it became so dark brown that no electric spark was seen. The concentration then determined by precipitating with a little electrolyte was 60~80 mg. of platinum per litre. After standing for several days to permit the larger platinum particles to settle, the sol was carefully siphoned off and diluted

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* This is the English translation of the paper which appeared in *Rev. Phys. Chem. Japan*, 10, 251 (1936).

1) G. Bredig and co-workers, *Z. physik. Chem.*, 31, 259 (1899); 37, 1, 323 (1901); 66, 162 (1909); 70, 34 (1909); 81, 385 (1912); *Ber.*, 37, 798 (1804) *etc.*

2) T. S. Price and A. D. Denning, *Z. physik. Chem.*, 46, 89 (1903); D. A. McInnes, *J. Am. Chem. Soc.*, 36, 878 (1914); J. Groh, *Z. physik. Chem.*, 88, 414 (1914); T. Iredale, *J. Chem. Soc.*, 119, 109 (1921), 121, 1536 (1922); H. V. Tartar and N. K. Schaffer, *J. Am. Chem. Soc.*, 50, 2604 (1928); M. A. Heath and J. H. Walton, *J. Phys. Chem.*, 37, 979 (1933) *etc.*

3) S. Horiba and T. Ichikawa, *Rev. Phys. Chem. Japan*, 1, 145 (1927); T. Ichikawa, *Z. physik. Chem.*, (B) 10, 299 (1930); S. Horiba, *Rev. Phys. Chem. Japan*, 11, 189 (1937); T. Kôsaki, *ibid.*, 12, 21 (1938); H. Matsuyama, *ibid.*, 12, 168 (1938) *etc.*

4 times. This stock solution was so stable without any addition of a protective colloid or peptizer that no precipitate was noticed after several months; and it never coagulated after the decomposition of hydrogen peroxide.

The hydrogen peroxide solution was a diluted Merk's 'Perhydrol'.

All the water used was a conductivity water prepared thus: twice distilled water was redistilled by means of a Pyrex condenser and then the air without CO_2 was passed for several days. All the vessels used were made of 'Telex' glass[4] and were steamed out.

Apparatus and Procedure.

In the thermal analysis in the liquid system, the measurement of the temperature change of the reaction system was made by means of a glass calorimeter as shown in Fig. 1. In the figure, A is a glass Dewar vessel holding about 100 c.c. of a solution, B a glass vessel which holds about 60 c.c., C a normal Beckmann's thermometer, D a glass stirrer rotating 300±20 times per minute, and E a heater with a platinum wire resistance movable up and down.

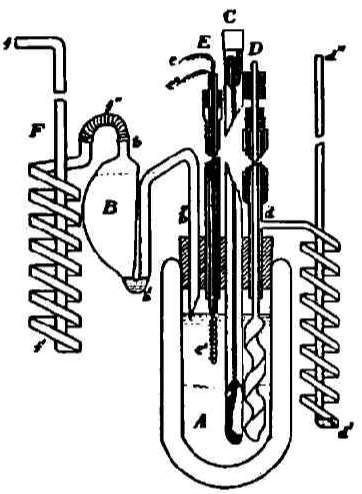

Fig. 1.

50 c.c. of platinum sol was introduced into A and a solution of hydrogen peroxide in B to let just 50 c.c. flow out of b''. The lid which supports B, C, D and E was put on A tightly and then f'' was connected. The whole apparatus was dipped in a thermostat at 30±0.002°C. The platinum sol in A was heated to almost the same temperature as that of the thermostat by E, and then E was drawn out to avoid the catalytic decomposition by it. After thermal equilibrium had been obtained about 1 hour later, hydrogen peroxide solution was siphoned off into platinum sol in A within 3-4 seconds, first blowing from f. Instantly they were mixed with each other and the reaction started. At the same moment, Beckmann's thermometer which was tapped automatically was read on. The initial concentration of hydrogen peroxide was determined in another flask by titration with standard potassium permanganate solution.

Calculation Method of Thermal Analysis.

The principle of the thermal analysis can be expressed by the following equation:

$$\frac{dT}{dt}-\frac{dT'}{dt}=\frac{Q}{W}\frac{dx}{dt}, \quad \cdots\cdots (1)$$

where $\frac{dT}{dt}$ is the temperature change in the reaction system, $-\frac{dT'}{dt}$ is the cooling velocity due to the temperature difference between a reaction system and its surroundings, *i.e.* the thermostat, $Q\cdot\frac{dx}{dt}$ is the heat quantity produced by the reaction per unit time (Q and $\frac{dx}{dt}$

4) The 'Telex' glass manufactured by Tokyo Electric Co. Ltd. is similar to 'Pyrex' in quality.

are the reaction heat and the reaction velocity respectively), and W the water equivalent of the reaction system.

Cooling Constant and Water Equivalent.

In the calculation of the reaction velocity and reaction heat according to equation (1), it is necessary to know $-\frac{dT'}{dt}$ and W which are particular to the reaction system, *i.e.* the apparatus. In this case the cooling follows Newton's law, that is, it is proportional to the temperature difference, ΔT, between the reaction system and the thermostat. This was empirically justified with some correction, θ or τ, caused by stirring heat or others.[5] Therefore,

$$-\frac{dT'}{dt}=K\cdot\Delta T-\theta \quad \cdots\cdots (2)$$

$$=K(\Delta T-\tau). \quad \cdots\cdots (2')$$

Thus, by the measurement of natural cooling velocity of the reaction system the cooling constant K and the correction term θ or τ can be obtained.

Let r represent the resistance of the platinum wire of the heater and i the intensity of the electric current transmitted through it, then the heat quantity per minute q' liberated by the current is $\frac{i^2r\times 60}{4.184}$ (cal.). Putting q' for $Q\cdot\frac{dx}{dt}$ in equation (1), we have

$$W=\frac{q'}{\frac{dT}{dt}+K(\Delta T-\tau)}. \quad \cdots\cdots (3)$$

Accordingly, the water equivalent W is obtained from the measurement of the rate of the temperature rise of the reaction system by electric heating.[6] The resistance of the heater r was measured preliminarily by a potentiometric method under the same condition as in the calculation of the water equivalent and was found to be 0.493 ohm. The values of K and W obtained are given in Table I.

Table I.

No.	τ (°C)	θ (°C/min.)	K[7] (*a*)	(*b*)	i (amp.)	W (cal.)	N.B.
1	0.019	0.00024	0.01393		0.8	116.84	pure water
2	12	18	1390		1.0	116.95	
3	18	20	1395	0.01391	0.8	116.57	solution after reaction
4			1397	1400	1.0	116.38	
5			1403	1394	0.8	116.45	
6			1385	1391	0.9	115.70	
7	18	20	1392	1397			

Mean values: $\tau=0.018$, $\theta=0.0002$, $K=0.0139$, $W=116.6$

5) $\frac{\theta}{\tau}=K$; θ is the rate of temperature rise by stirring; τ is the temperature difference between the reaction system and the thermostat at thermal equilibrium, being due to stirring heat.

6) The platinum wire of the heater is dipped in the solution in this case and not in case of the reaction. Consequently, the water equivatent for the reaction must be exactly $W-0.014$, because the weight of the platinum wire is 0.46 gm. and the specific heat is 0.0312. This correction, however, is negligible as compared with the value of W.

7) As to the value of K, (*a*) was obtained from graphical method and (*b*) from calculation. *See*, S. Horiba and K. Sato, *Rev. Phys. Chem. Japan*, 6, 25 (1932).

Reaction Velocity.

Substituting equation (2′) in the fundamental formula (1), we have

$$\frac{dT}{dt}+K(\Delta T-\tau)=\frac{Q}{W}\cdot\frac{dx}{dt}. \quad \cdots\cdots (4)$$

As $\frac{dT}{dt}$ is the inclination of the reaction curve ($\Delta T\sim t$ curve), the value of $\frac{Q}{W}\cdot\frac{dx}{dt}$ can be easily obtained from equation (4). In this case W is known and Q can be obtained as shown below; hence the reaction velocity $\frac{dx}{dt}$ at a certain time can be calculated. Even if W and Q are unknown, both are constants and so the plot of $\frac{Q}{W}\cdot\frac{dx}{dt}$ for a time t makes the reaction velocity curve.

If the reaction is of the first order,

$$\frac{dx}{dt}=k_1(a-x)=k_1a\times e^{-k_1t}, \quad \cdots\cdots (5)$$

where k_1 is the velocity constant and a is the initial concentration. Putting (5) in equation (4) and taking logarithms, we have

$$\log\left\{\frac{dT}{dt}+K(\Delta T-\tau)\right\}=\log\frac{Q}{W}\cdot\frac{dx}{dt}=\log\frac{Qk_1a}{W}-\frac{k_1t}{2.303}. \quad \cdots\cdots (6)$$

Accordingly, plotting the value of $\log\frac{Q}{W}\cdot\frac{dx}{dt}$ for a time t, a straight line will be obtained and the slope of this line will give k_1.

Reaction heat.

From equations (1) and (2), the following equation is obtained:

$$\frac{dT}{dt}+K\Delta T-\theta=\frac{Q}{W}\cdot\frac{dx}{dt}. \quad \cdots\cdots (4')$$

Integrating this equation from $t=0$ to $t=t$, a certain time after the completion of the reaction, we have

$$\begin{aligned}Q&=\frac{W}{a}\left\{\int_0^t dT+K\int_0^t \Delta T\cdot dt-\theta t\right\}\\&=\frac{W}{a}\left\{(\Delta T)_{t=t}+K\cdot S-\theta t\right\}.\end{aligned} \quad \cdots\cdots (7)$$

Hence, if the value of $S=\int_0^t \Delta T\cdot dt$ is calculated by the graphical integration of the $\Delta T\sim t$ curve, the reaction heat Q can be obtained.

In the case of the first order reaction, the intersection of $\log\frac{Q}{W}\frac{dx}{dt}\sim t$ line with the ordinate represents $\log\frac{Qk_1a}{W}$ as seen from equation (6). Accordingly, from the initial concentration a, the velocity constant k_1, and the water equivalent W, the reaction heat Q can be calculated.

Experimental Results and their Consideration.

One of the results obtained is given in Table II. The curve obtained by plotting $\Delta T(=T-T_0')$ for t is shown as (a) in Figs. 3, 4, 6, 7 and 8.

Table II.

(a) Series I, Expt. 4. (Dec. 3, 1935)
Pt-sol 10c.c.
H_2O_2 0.029 g.-mol/litre
30°C (room temp. 18~22°C)

T (°C)	t (min)-(sec)	T (°C)	t (min)-(sec)	T (°C)	t (min)-(sec)
2.499		2.810	14 • 45	2.868	46 • 30
↑	12	820	15 • 40	862	48 • 00
510	28	830	16 • 34	858	50 • 00
520	52	840	17 • 50	852	52 • 00
530	1 • 12	850	19 • 00	844	54 • 00
540	30	857	20 • 00	838	56 • 00
550	54	861	21 • 00	830	58 • 00
560	2 • 12	867	22 • 00	825	60 • 00
570	30	872	23 • 00	814	63 • 00
580	51	876	24 • 00	806	66 • 00
590	3 • 12	879	25 • 00	794	69 • 00
600	31	881	26 • 00	784	72 • 00
610	53	883	27 • 00	776	75 • 00
620	4 • 16	887	28 • 00	766	78 • 00
630	38	888	29 • 00	757	81 • 00
640	5 • 03	889	30 • 00	748	84 • 00
650	32	890	31 • 00	738	87 • 00
670	6 • 19	890	32 • 00	729	90 • 00
680	44	890	33 • 00	721	93 • 00
690	7 • 09	890	34 • 00	712	96 • 00
700	34	889	35 • 00	706	99 • 00
710	8 • 07	888	36 • 00	698	102 • 00
720	38	887	37 • 00	690	105 • 00
730	9 • 07	885	38 • 00	679	110 • 00
740	42	883	39 • 00	668	115 • 00
750	10 • 16	881	40 • 00	660	120 • 00
770	11 • 37	879	41 • 00	650	125 • 00
780	12 • 15	877	42 • 00	640	130 • 00
790	13 • 00	875	43 • 30	622	140 • 00
800	52	871	45 • 00	608	150 • 00

T_0=2.500

(b) Series IV, Expt. 3. (Feb. 5, 1936)
Pt-sol 20c.c.
H_2O_2 0.028 g.-mol/litre
30°C (room temp. 20°C)

T (°C)	t (min)-(sec)	T (°C)	t (min)-(sec)
2.500		2.840	3 • 56
↑	05	850	4 • 06
510	11	860	19
520	17	870	31
530	24	880	44
540	29	890	56
550	34	900	5 • 11
560	41	910	30
570	45	920	49
580	51	930	6 • 08
590	57	940	33
600	1 • 02	950	7 • 00
610	07	958	30
620	13	964	8 • 00
630	19	970	30
640	25	973	9 • 00
650	31	977	30
660	36	979	10 • 00
670	43	981	30
680	49	982	11 • 00
690	55	983	30
700	2 • 01	983	12 • 00
710	08	983	30
720	14	983	13 • 00
730	21	981	14 • 00
740	29	978	15 • 00
750	37	973	16 • 00
770	52	962	18 • 00
780	3 • 00	951	20 • 00
790	09	938	22 • 00
800	18	928	24 • 00
810	27	916	26 • 00
820	36	903	28 • 00
830	45	893	30 • 00

T_0=2.500

Using the values of $\frac{Q}{W}\cdot\frac{dx}{dt}$ and $\log\frac{Q}{W}\cdot\frac{dx}{dt}$ obtained from this curve according to equation (4), as an example in Table III, the reaction velocity curve was drawn as (b) in Figs. 3, 4, 7 and 8. And the $\log\frac{Q}{W}\cdot\frac{dx}{dt}\sim t$ curve is seen nearly linear as (c) in Figs. 3, 4, 6, 7 and 8, and from its slop k_1 was obtained.

Table III.

(a)

t (min.)	ΔT (°C)	$K(\Delta T-\tau)$	$\frac{dT}{dt}$	$\frac{Q}{W}\frac{dx}{dt}$	$\log\frac{Q}{W}\frac{dx}{dt}$	t (min.)	ΔT (°C)	$K(\Delta T-\tau)$	$\frac{dT}{dt}$	$\frac{Q}{W}\frac{dx}{dt}$	$\log\frac{Q}{W}\frac{dx}{dt}$
0	−0.001	−0.0003	+0.0269	+0.0266	$\bar{2}\cdot 425$	26.0	+0.382	+0.0050	+0.0026	+0.0076	$\bar{3}\cdot 883$
1.0	+0.024	+0.0001	271	272	434	27.0	384	51	22	73	861
2.0	052	04	271	275	435	28.0	386	51	18	69	838
3.0	083	08	293	301	479	29.0	388	51	13	64	807
4.0	112	12	267	279	446	30.0	389	51	09	60	780
5.0	137	16	250	266	425	32.0	390	51	04	55	744
6.0	161	19	240	259	414	34.0	390	51	−0.0001	50	703
7.0	185	22	227	249	398	36.0	389	51	09	42	626
8.0	207	25	210	235	373	38.0	387	51	18	33	519
9.0	227	28	188	216	336	40.0	383	50	21	29	462
10.0	245	31	170	201	301	42.0	379	50	25	25	398
11.0	261	33	153	186	270	44.0	374	49	27	22	342
12.0	276	35	142	177	249	46.0	368	48	28	20	301
13.0	290	37	128	165	219	48.0	363	48	30	18	255
14.0	301	39	117	156	193	50.0	358	47	31	16	204
15.0	313	40	106	146	166	55.0	341	45	33	12	079
16.0	323	42	096	138	140	60.0	325	43	34	09	
17.0	333	43	88	131	119	65.0	308	41	35	6	
18.0	342	44	79	123	090	70.0	292	38	33	5	
19.0	349	45	71	116	066	75.0	276	36	32	4	
20.0	356	46	64	110	043	80.0	260	33	30	3	
21.0	362	47	56	103	015	85.0	238	30	29	1	
22.0	367	48	50	098	$\bar{3}\cdot 992$	90.0	229	28	27	1	
23.0	372	48	44	92	968	100.0	203	25	25	0	
24.0	376	49	38	87	942	110.0	179	22	22	0	
25.0	379	50	30	80	902	120.0	160	19	20		

$k_1 = 0.0592$

(b)

t (min.)	ΔT (°C)	$K(\Delta T-\tau)$	$\frac{dT}{dt}$	$\frac{Q}{W}\frac{dx}{dt}$	$\log\frac{Q}{W}\frac{dx}{dt}$	t (min.)	ΔT (°C)	$K(\Delta T-\tau)$	$\frac{dT}{dt}$	$\frac{Q}{W}\frac{dx}{dt}$	$\log\frac{Q}{W}\frac{dx}{dt}$
0	0.000	−0.0003	+0.0920	+0.0917	$\bar{2}\cdot 962$	6.5	+0.439	+0.0058	+0.0230	+0.0288	$\bar{2}\cdot 459$
0.5	+0.040	+0.0003	1040	1043	$\bar{1}\cdot 018$	7.0	450	60	185	245	389
1.0	098	11	1200	1211	083	7.5	458	61	150	211	324
1.5	150	18	1000	1018	008	8.0	464	62	130	192	283
2.0	196	24	0920	0944	$\bar{2}\cdot 975$	8.5	470	63	105	168	225
2.5	241	28	808	836	922	9.0	474	63	080	143	155
3.0	280	36	720	756	879	9.5	477	64	50	114	057
3.5	315	41	640	681	833	10.0	479	64	40	104	017
4.0	344	45	540	585	767	11.0	481	64	20	084	$\bar{3}\cdot 924$
4.5	370	49	460	509	707	12.0	483	64	0	64	806
5.0	391	52	400	452	655	13.0	482	64	−0.0015	49	690
5.5	410	54	360	414	617	14.0	481	64	30	34	531
6.0	427	56	280	336	526	15.0	478	64	60	04	

$k_1 = 0.2925$

Five series of the experiments were carried out as follows (*cf.* Table IV):

I and II. The concentration of hydrogen peroxide was kept constant, and that of platinum sol was varied. The activity of platinum sol varied during the stock as proved in Series III. Series II were carried out on the sol, whose activity became extremely high in half a month's stock after series I.

III. The change of activity of the colloid caused with aging was examined.

IV and V. The concentration of hydrogen peroxide was changed. The time

Table IV.

Expt. No.		Date	Conc. of H_2O_2 ratio	Conc. of H_2O_2 $\left(\frac{\text{g.-mol}}{\text{litre}}\right)$	Conc. of Pt-sol. cc. of stock soln.	Conc. of Pt-sol. $\left(\frac{\text{g.-atom}}{\text{litre}} \times 10^{-6}\right)$ (approx.)	a (min.)	k_1 (min.$^{-1}$)	Q $\left(\frac{\text{Cal.}}{\text{g.-mol}}\right)$
I	1	Dec. 5, 1935.	3.7	0.029	25	13–20	1	0.4677	23.946
	2	Nov. 30	,,	29	20	10–15	1.2	2190	24.474
	3	Dec. 2	,,	29	15	7–11	2	1532	24.467
	4	,, 3	,,	29	10	5– 7	3	0592	23.880
	5	,, 4	,,	29	5	3– 4	4	0210	
II	1	,, 17	,,	29	12.5	6– 9	1	1753	24.193
	2	,, 18	,,	29	10	5– 7	2	0986	23.613
	3	,, 16	,,	29	7.5	4– 6	3	0507	24.163
	4	,, 19	,,	29	5	3– 4		0267	
III	1	,, 3 } 15 days	,,	29	10	5– 7	3	0592	(23.880)
	2	,, 18 } 8 ,,	,,	29	,,	,,	2	0986	(23.613)
	3	,, 26 } 39 ,,	,,	29	,,	,,	2	1163	23.344
	4	Feb. 3	,,	29	,,	,,	2	0686	23.780
	1′	Dec. 4 } 15 ,,	,,	29	5	3– 4	4	0210	
	2′	,, 19 } 8 ,,	,,	29	,,	,,		0267	
	3′	,, 27	,,	29	,,	,,	3	0269	
IV	1	Feb. 5, 1936.	8	62	20	10–15	1	(2628)	23.632
	2	,, ,,	4	31	,,	,,	,,	3351	23.984
	3	,, ,,	3.5	27	,,	,,	,,	2925	23.653
	4	,, 4	3	24	,,	,,	,,	3335	24.045
	5	,, 6	2.5	20	,,	,,	,,	3346	24.042
	6	,, 4	2	16	,,	,,	,,	3321	23.502
	7	,, ,,	1	08	,,	,,	,,	3356	23.615
V	1	,, 20	8	63	10	5– 7	2	(0753)	23.525
	2	,, ,,	5	38	,,	,,	3	0675	23.683
	3	,, 19	3	24	,,	,,	2	0610	23.568
	4	,, 21	2	16	,,	,,	,,	0914	23.990
								mean	23.886

(Note) (1) The stock solution of Pt-sol No. 2. prepared on Nov. 12, 1935 was used for Series I, II, III & V, and No. 3 prepared on Feb. 3, 1936 for Series IV.

(2) The concentrations of H_2O_2 and Pt-sol indicate those at the reaction, *i.e.* those after the mixing of both solutions.

of the reaction was shortened and both series were completed within a few days to lessen the change of the activity. Series V were examined with the object of considering the initial part of the reaction.

(1) Reaction Type.

The reaction always proceeds as shown schematically in Fig. 2: it proceeds in the two stages—*the initial stage* (ab) and *the later stage* (cde). The later stage, which is the main part of the reaction, is exactly of the first order (for the line c′ d′ e′ is straight), and before this stage a special stage appears.

It has been admitted that the catalytic decomposition of hydrogen peroxide by metalic colloids is either of the first order or nearly of the first order with some deviation. Even in the present experiments, if k_1 is calculated by an ordinary method $\left(k_1=\frac{1}{t}\ln\frac{a}{a-x}\right)$ neglecting the initial stage, it does not become constant and the reaction does not exactly appear to be of the first order over the whole region. By the ordinary titration method the initial stage will never be noticed, because this stage is too short for the time interval of measurements. But it is interesting to mention that by the thermo-analytical method the initial stage was found, which will be discussed later.

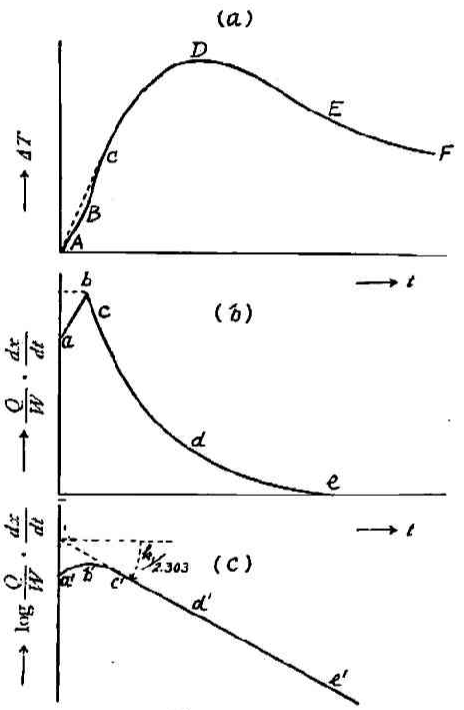

Fig. 2.

(2) The Effect of Concentration of Platinum Sol.

From the experimental results of Series I and II as shown in Figs. 3 and 4, the duration of time of the initial stage a (the 7th column in Table IV) is decreased as the concentration of the sol is increased. The reaction velocity constant k_1 is nearly proportional to the square of the concentration of the sol, as seen in Fig. 5.[8]

8) The deviation of the plots of Expts. 1 and 2 from the straight line of Series I can be explained by taking into account the increase in the activity with aging and that Expt. 2 was carried out first and Expt. 1 last in this series.

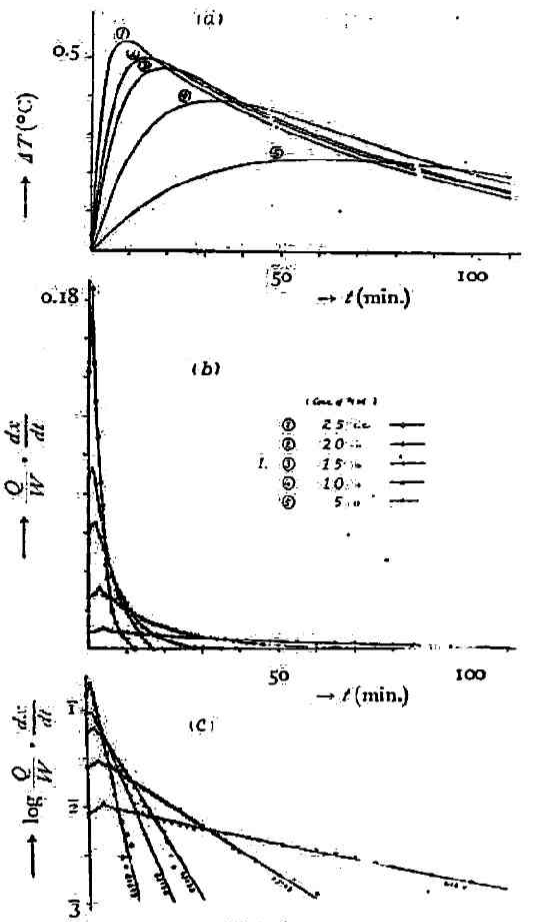

Fig. 3.

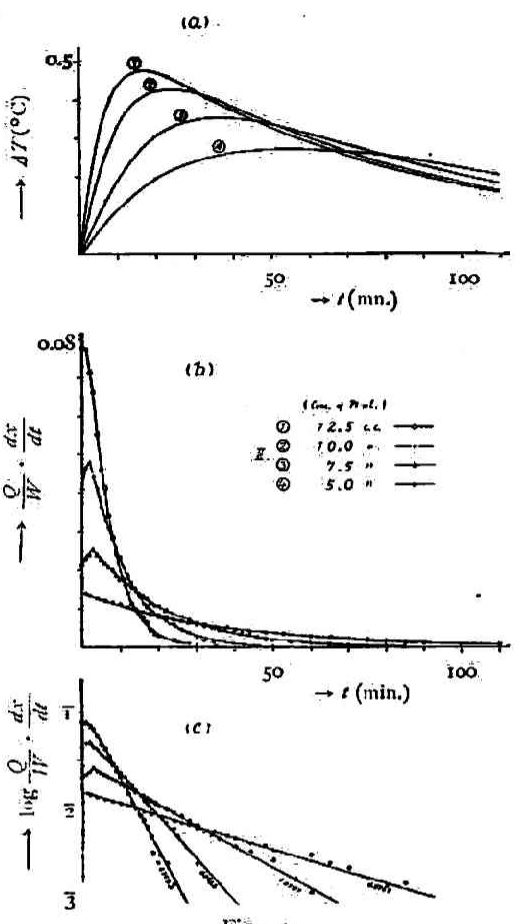

Fig. 4.

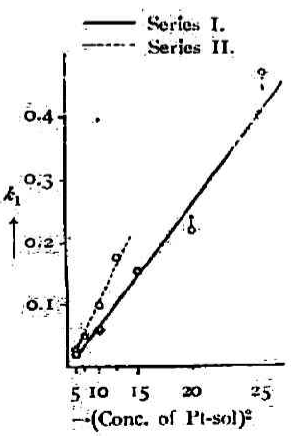

Fig. 5.

Generally speaking, in the case of colloidal catalysis, the reaction velocity is not proportional to the amount of catalyst, *i.e.* the concentration of the sol, and the following relation holds, that is,

$$\frac{k}{k'}=\left(\frac{c}{c'}\right)^n,$$

where k and k' are the velocity constants for c and c', the concentrations of the sol. For the values of n, Bredig and his co-workers[9] have obtained 1.3～1.6, 1.1～1.4 and 1 in the decompositions of hydrogen peroxide by Pt-sol, Au-sol and Ir-sol respectively. In the present experiment, it was as high as 2.

9) *loc. cit.*

(3) The Change in the Activity of the Colloid with Time.

In the comparison between the experimental results Series I and II obtained with 5 c.c. and 10 c c. of the sol, it was found that the reaction velocity was larger in Series II than in Series I. To make clear this change in the activity, the experimental results with some addition are shown in Fig. 6 as Series III. It was found that the activity of colloid increased with aging, reached the maximum and then diminished. And it is to be noted that the duration of the initial stage α tends to become short with the time.

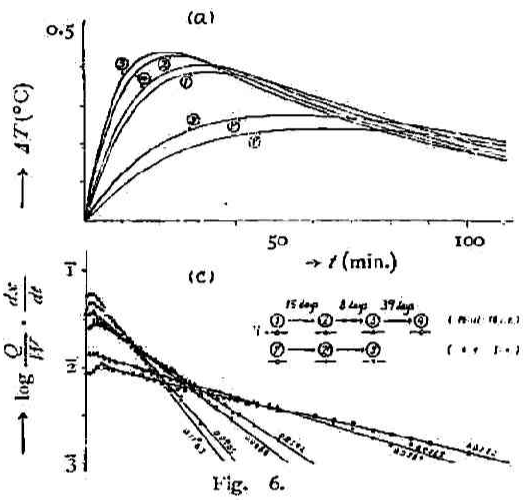

Fig. 6.

It is interesting that in colloidal catalysis the activity does not gradually diminish as in the common case of heterogeneous catalysts but rather increases to the maximum. This result G. Rocasolano[10] has attributed to the effect of oxygen contained in the sol. S. Rusznyak[11] has found in the decomposition of hydrogen peroxide by Ag-sol that when the dispersity is high, *i.e.* the size of the colloidal particle is small, the activity is also low. This relation between the particle size and activity can not be applied as a general rule to colloidal catalysis, because his experiments were carried out with the sol which was prepared chemically by reducing method and seemed to contain many other substances acting as a poison; but if we regard his results as applicable to our case, we may think that the increase in activity with aging is due to the growth of the colloid particles. However, it is probably inferred that the phenomena is rather due to the change in the surface nature of the colloid.

A more definite interpretation of this phenomenon will require further experiments. And the relation between the size of the particle of a colloid and its activity is an interesting question in the colloidal catalysis. The fact that the activity falls off after a long time as in Expt. 4 may be ascribed to the decrease in the concentration of the sol by precipitation.

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10) G. Rocasolano, *Compt. rend.*, **170**, 1502; 171, 301 (1920).
11) S. Rusznyak, *Z. physik. Chem.*, **85**, 681 (1913).

(4) The Effect of Concentration of Hydrogen Peroxide Solution.

The experimental results (Series IV and V) obtained with various concentrations of hydrogen peroxide are shown in Figs. 7 and 8.[12]

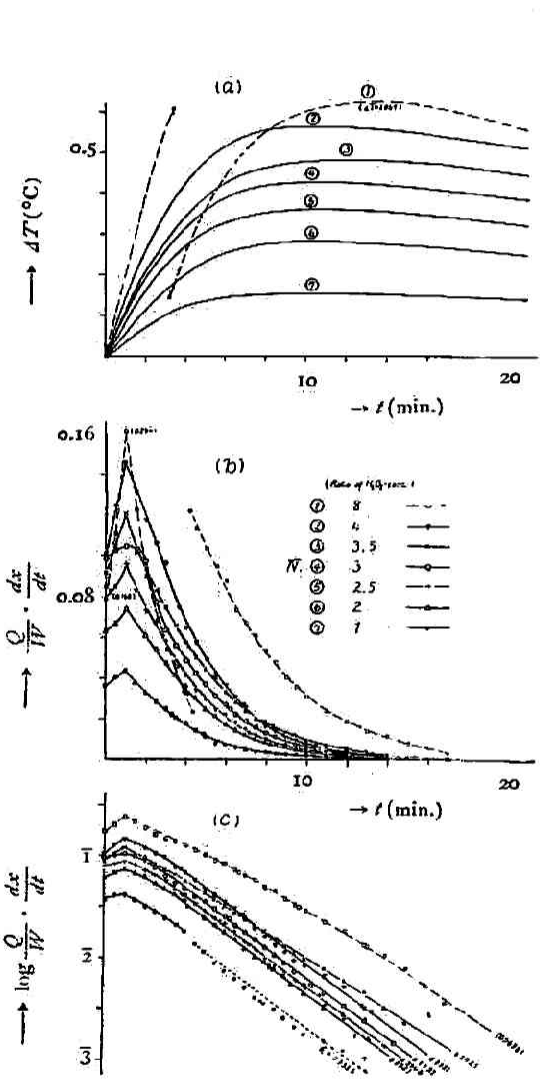

Fig. 7.

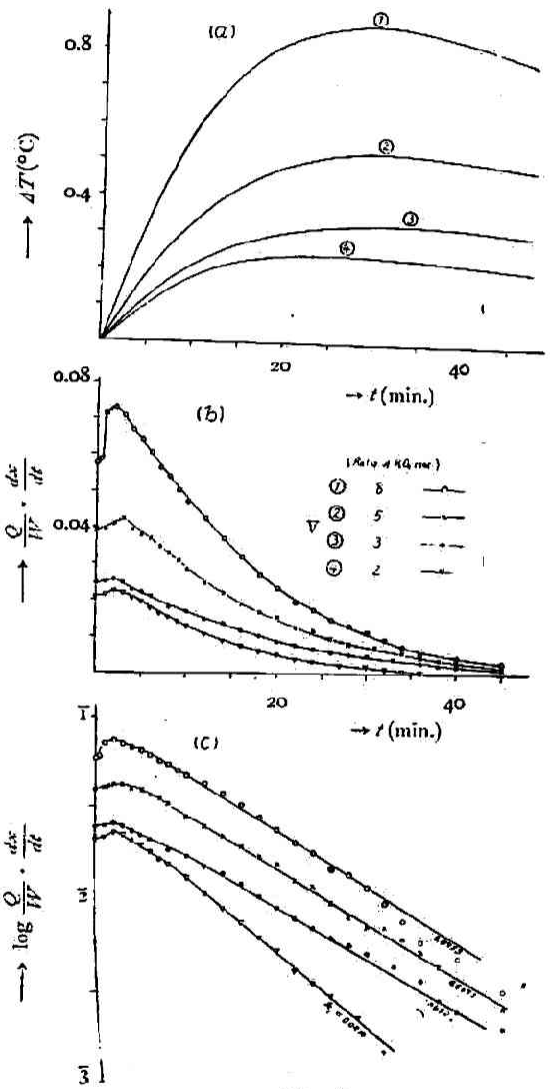

Fig. 8.

It is seen from the reaction velocity curve that the initial reaction velocity is nearly proportional to the initial concentration of hydrogen peroxide, and that

12) In all the experiments, except Expt. 1 in Series IV and V, the temperature difference (ΔT) of the reaction system is below 0.5°C, and within this temperature the effect of the velocity constant due to temperature rise may be negligible. Expt. 1 in Series IV and V was carried out with temperature difference over 1°C, only to examine the initial part of reaction. Deviation of k_1 in Expt. 3 in Series IV is probably ascribed to some error of the concentration of the sol.

each reaction ends almost at the same time. Next, that the linear part of the $\log \frac{Q}{W} \cdot \frac{dx}{dt} \sim t$ curve runs in parallel shows that the reaction velocity constant k_1 agrees well with one another. The duration of the initial stage α is about 1 min. in Series IV and 2–3 min. in Series V.

(5) The Heat of Decomposition of H_2O_2.

The reaction heat Q calculated according to equation (7) is 23.9±0.5 Cal. per 1 g.-mol, being in considerably good agreement as shown in the last column of Table IV.

Let us compare this result with those of other investigators. Matheson and Mass[13] obtained 23.45 Cal. as the decomposition of hydrogen peroxide solution with small particles of MnO_2 by means of adiabatic calorimeter. Roth, Gran and Meichsner[14] obtained 23.42 Cal. (at 20°C.) for a 97.27% solution and 22.64 Cal. for 0.33% solution. From thermo-chemical data[15], $-22 \sim -25$ Cal. was calculated as the heat of formation from water and oxygen gas. In comparison with these values it is seen that the author's value is proper.

(6) The Initial Part of the Reaction.

As to the initial part of the reaction, the deviation of the curve from the first order is very slight. But it is ascribed not to the errors of the apparatus, such as the time lag of Beckmann's thermometer, absorption of heat by the calorimeter, *etc.*, but to the reaction itself as is clear from the following three points.

(1) The deviation can not be noticed in the case of electric heating.

(2) When the reaction heat was calculated from the intersection of the extension of the straight part in the $\log \frac{Q}{W} \cdot \frac{dx}{dt} \sim t$ curve with the ordinate under the assumption that the reaction proceeds according to the first order from the beginning, the value obtained is generally larger than that obtained before, and there is no agreement in the value of each experiment.

(3) As to the duration of the initial stage α, inspecting from the results of Series I and II, it is found that the higher the concentration of the sol is, the shorter the duration becomes. If the difference among the duration is to be regarded as due to the initial reaction velocity, that is, the rate of temperature rise, the error to be caused by the apparatus also should be taken into account. But, as seen from the results of Series IV and V, even though the initial reaction velocity is different, when the concentration of the sol is definite, α is nearly

13) G. L. Matheson & O. Mass, *J. Am. Chem. Soc.*, **51**, 674 (1929).

14) W. A. Roth, R. Gran u. A. Meichsner, *Z. anorg. Chem.*, **193**, 165 (1930).

15) M. Belthelot, *Compt. rend.*, **90**, 331, 897 (1880); R. de Forcrand, *ibid.*, **130**, 1250 (1900); J. Thomson, *Thermochemische Untersuchungen, etc.*

constant. Morever, in comparison between the results of these two series it is found that variation in the concentrations of the sol leads to the different value of α even in the same initial velocity. Therefore, it is inferred that α is affected not by the rate of temperature rise but by the reaction itself, and probably it is related to the amount of the colloid.

The reaction velocity curve of the initial stage is indefinite in each experiment, being not always linear. Therefore, the nature of the reaction of this stage can not be made clear. The appearance of this stage may depend upon the adsorption of hydrogen peroxide on the surface of colloid, namely, to reach the adsorption equilibrium in liquid system may need a considerable time, which will be the duration of initial stage α. And in colloidal system the electric double layer of its surface will play an important rôle for the adsorption (diffusion). This presumption is not certain and theoretical consideration on this colloidal catalysis will be required.

Summary.

1) By the method of thermal analysis the catalytic decomposition of hydrogen peroxide solution by platinum sol has been studied, especially the effect of the concentration of platinum sol and that of hydrogen peroxide.

2) It has been found that the reaction proceeds in two stages: the initial stage and the later stage. The duration of the initial stage is practically independent of the concentration of hydrogen peroxide and is nearly in inverse proportion to concentration of the sol. The later stage, which is the main part of reaction, is of the first order with respect to hydrogen peroxide and the reaction velocity constant is proportional to the square of the concentration of the sol, *i.e.*,

$$\frac{dx}{dt} = k_1 (H_2O_2), \qquad k_1 \propto (Pt\text{-}sol)^2.$$

3) The activity of the colloidal catalyst increases at first with aging.

4) The value of the decomposition heat of hydrogen peroxide has been found to be 23.9 Cal. per g.-mol.

In conclusion, the author has great pleasure in expressing his sincere thanks to Prof. S. Horiba for his valuable guidance during the course of this research.

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